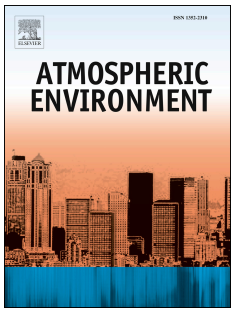

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AUTHOR CONTRIBUTIONS

Courtney D. Grimes: Conceptualization, Methodology, Investigation, Writing-Original Draft preparation **Joseph M. Conny**: Resources, Supervision, Writing-Reviewing and Editing **Russell R. Dickerson**: Supervision, Funding Acquisition

Evaluation of Thermal Optical Analysis (TOA) using an aqueous binary mixture

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KEYWORDS. Black carbon, elemental carbon, organic carbon aerosol, thermal optical transmission analysis, TOT

ABSTRACT. Thermal-Optical Analysis (TOA), a commonly implemented technique used to measure the amount of particulate carbon in the atmosphere or deposited on a filter substrate, distinguishes organic carbon (OC) from elemental carbon (EC) through the monitoring of laser light, heating, and measuring evolved carbon. Here, we present a method to characterize the TOA transmission method with an aqueous binary mixture containing EC and OC that can easily be deposited onto a filter at low volumes. Known amounts of EC and OC were deposited onto a quartz-fiber filter and analyzed with different temperature protocols. Results with the NIST-EPA-C temperature protocol agreed with the reference values to better than 2 % for EC, OC, total carbon (TC), and EC/TC. Indicated TC for all temperature protocols was within 5 % of the reference value while all protocols reproduced EC/TC ratios with an uncertainty less than 10 %.

1. Introduction

Black carbon (BC), a form of atmospheric particulate matter (PM), influences Earth's radiative budget, local visibility, and adversely impacts human health (*1*). BC is a component of soot with graphite-like structures, where the particles are chemically inert. As a refractory material, BC is also known as elemental carbon (EC). Due to different combustion conditions, atmospheric mixing and aging, these light absorbing particles often are combined with organic carbon (OC), mineral dust, and nitrates (*2*). There is much discrepancy associated with the quantification of BC among different techniques. Some of the filter-based techniques include optical methods such as aethalometry (*3*) and the combination of optical and thermal based characterization (*4*) such as thermal-optical analysis (TOA). Since TOA functions optically as well as thermally, it is an appropriate method for determining the mass of BC as a light-absorbing material in the atmosphere. TOA is known to be problematic because different temperature protocols provide inconsistent results for BC, and measurements can disagree greatly with other BC quantification techniques (*5-8*). This study presents a new technique incorporating a binary solution of known concentrations of OC and BC to evaluate TOA methods involving different temperature protocols. The technique presented here could serve as a calibration method for characterizing TOA.

A Sunset Thermal-Optical Carbon Aerosol Analyzer* was used in this work (Sunset Lab, Tigard, OR). A section from a quartz-fiber filter is placed on a quartz boat in the path of a 670 nm laser beam to monitor the change in transmittance through the filter as the sample is heated. The technique is known as thermal-optical transmission analysis when laser transmission is used and thermal-optical reflection analysis when reflection is utilized. Carbon species are evolved

from the quartz filter in the front oven upon heating and converted to carbon dioxide in a MnO_2 oxidation back oven at 870 ^oC. The first phase of the analysis occurs in an oxygen-free helium environment, where some organic compounds are pyrolytically converted to EC in the front oven. As OC pyrolyzes and becomes darker, laser transmittance through the filter decreases. The second phase occurs in an oxygen/helium environment where the pyrolyzed OC and EC are oxidized to carbon dioxide and laser transmittance through the filter increases. This CO_2 is reduced to methane in a 500 ^oC Raney nickel catalyst oven before passing into a flame ionization detector. The instrument distinguishes the OC from EC when the transmittance of the filter returns to its original value – the split point. Carbon detected after the split point is measured as BC that was native to the sample. Following the detection of carbon, a known amount of methane is injected into the sample oven, then oxidized and reduced back to methane, which is the method's internal standard (*9-12*).

2. Methods

A 1 mg/mL suspension of Cab-o-Jet 200 (19.92 % mass fraction, Cabot Corp.) was prepared with deionized water (*13*). The carbon black material acts as an EC surrogate and has been well characterized (*14, 15*). Prior research with TOA showed that this material is comprised of approximately 96 % EC and 4 % OC. A separate 4.0 mg/mL solution of sucrose was prepared to act as an OC surrogate. Sucrose is a suitable material for OC for ambient air organic aerosol because a substantial amount of its carbon pyrolyzes (chars) when heated in an inert atmosphere. From the two separate EC and OC preparations, a 10.0 mL binary mixture was prepared, where 7.0 mL was the OC solution and 3.0 mL was the EC suspension. A syringe was used to deposit 10.0 µL aliquots onto a 1.00 cm^2 quartz filter. The filter remained in the front oven until it was dry. Measurements of the binary mixture were taken with different temperature protocols. The

72 concentrations of EC, OC, TC and EC/TC ratios were recorded. Details concerning the
73 parameters of the different protocols are provided in Results/Discussion.

74 **3. Results and Discussion**

75 Tables 1 and 2 provide the temperature steps and residence times for the protocols developed
76 between the National Institute of Standards and Technology (NIST) and the Environmental
77 Protection Agency (EPA), and are modified versions of the NIOSH method. The temperature
78 protocols include NIST-EPA-A, NIST-EPA-B, NIST-EPA-C and Quartz. The Quartz protocol
79 (Table 2) was developed by the manufacturer early on and is based, in part, on work by Birch
80 and Cary (*12*) which has also led to the NIOSH 5040 method (*16*). Background research for the
81 NIST-EPA-A, NIST-EPA-B and NIST-EPA-C methods is given in Conny et al. 2007 (*17*). The
82 well-known Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol is
83 utilized primarily for thermal optical reflectance, and is not appropriate the thermal optical
84 transmittance instrument used in this work. The temperature steps for the IMPROVE protocol
85 are significantly lower than the protocols used in this work, and may not evolve all of the OC
86 (*18*).

87 **Table 1.** Temperature steps and residence times for the NIST-EPA-A,-B and -C protocols.

Carrier Gas (step)	Temperature (^{o}C)			Residence Time (s)		
	A	B	C	A	B	C
He (1)	200	200	200	60	60	60
He (2)	400	400	400	60	60	60
He (3)	600	600	600	60	60	60
He (4)	830	830	785	150	73	150
He+O_2 (1)	550	380	550	60	60	60
He+O_2 (2)	620	484	620	60	60	60
He+O_2 (3)	690	588	690	45	45	45
He+O_2 (4)	760	692	760	45	45	45
He+O_2 (5)	830	796	830	45	45	45
He+O_2 (6)	900	900	900	180	90	90

88

89 **Table 2.** Temperature steps and residence times of the Quartz protocol.

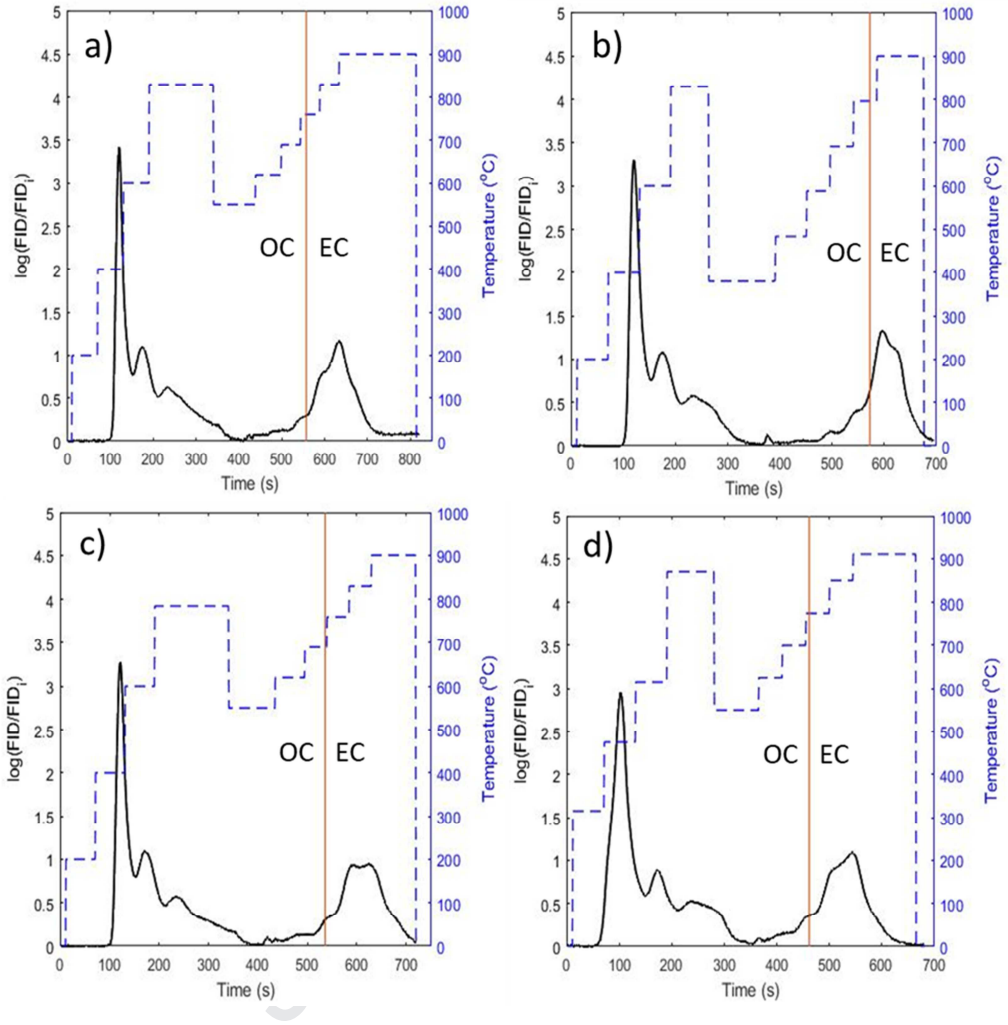
Carrier Gas (step)	Temperature (^{o}C)	Residence Time (s)
He (1)	315	60
He (2)	475	60
He (3)	615	60
He (4)	870	90
He+O_2 (1)	550	45
He+O_2 (2)	625	45
He+O_2 (3)	700	45
He+O_2 (4)	775	45
He+O_2 (5)	850	45
He+O_2 (6)	910	120

90

91 The NIST-EPA methods were derived from response surface models created from a factorial
92 experimental design involving temperature, duration of the high temperature step, and the
93 increase in heat in the He-Ox phase (*6*).These protocols were designed to deal with the split point
94 for differing sample types. Response surface models were calculated for absorption cross
95 sections of pyrolyzed OC and EC. The models revealed the step temperatures and durations, and
96 in the case of step 4 (final helium step), a range of possible step temperatures that ensures OC
97 charring is minimized to avoid OC being measured as EC by the instrument after the split point.
98 The primary differences between NIST-EPA-A and NIST-EPA-B are the step 4 duration times
99 and first step in the He-Ox phase. In comparison to NIST-EPA-A, the NIST-EPA-C protocol has
100 a relatively low temperature for step 4 in helium. The NIST-EPA-C protocol is considered
101 suitable protocol for a variety of sample types (high-charring and low-charring) (*17*). Examples
102 of temperature profiles, split points and FID responses are shown in Figures 1a-d.

103 **Figure 1.** Thermograms produced in response to the binary solution with a reference TC value of
104 15.03 μg/cm^2 and EC/TC ratio 0.213. The red solid line is the split point, the blue dashed lines
105 are the temperature steps. The black solid line is the FID response. Thermograms using (a)
106 NIST-EPA-A (reported values of TC=15.19 μg/cm^2 and EC/TC=0.215); (b) NIST-EPA-B

(reported TC=14.89 μg/cm^2 and EC/TC=0.209); (c) NIST-EPA-C (reported values of TC=15.17 μg/cm^2 and EC/TC=0.222); (d) Quartz (reported values of TC=15.51 μg/cm^2 and EC/TC=0.218).



Per 10 μL aliquot of the binary mixture, 11.86 ± 0.21 ($\bar{x} \pm s$) μg of OC and 3.18 ± 0.17 μg of EC were deposited onto the 1.00 cm^2 quartz filters, with a total carbon of 15.04 ± 0.83 μg. The calculated EC/TC ratio was 0.211 ± 0.012. This ratio allows for simple numerical comparison amongst the different protocols, and it is important for the determination of optical properties of ambient aerosols. These are the calculated reference values with propagated error. The reference values consider the 96 % EC composition of the surrogate material determined with prior

117 research (*15*). Multiple runs and blanks of deionized water were performed for each temperature
118 protocol. Averages and standard deviations of OC, EC, TC and EC/TC for the different
119 temperature protocols and number of replicates are presented in Table 3. Reference values in
120 Table 3 are amounts in the 10 µL aliquot from the binary mixture.

121 When compared to the reference values, the NIST-EPA-C protocol produced results for OC,
122 EC, TC and EC/TC which had an error of less than 2 % for all measurements. However, the
123 standard deviations are relatively high for EC but low for TC. NIST-EPA-C reported the highest
124 coefficient of variation for the OC component while NIST-EPA-B reported the largest
125 coefficient of variation for the EC component. All protocols reported average TC values within
126 0.5 µg (< 3 %) of the calculated reference TC value.

127

128 **Table 3.** Averages and standard deviations of OC, EC, TC and EC/TC for different temperature
129 protocols compared to the calculated reference values. Uncertainties of the reference values are
130 propagated errors from glassware and the balance used for volume and mass measurements. The
131 numbers of replicates are given by n.

	NISTEPA-A (n = 6)	NISTEPA-B (n = 3)	NISTEPA-C (n = 6)	Quartz (n = 5)	Reference
OC ($\mu g/cm^2$)	11.512 ± 0.717	11.567 ± 0.523	11.845 ± 1.043	11.294 ± 0.736	11.86 ± 0.21
EC ($\mu g/cm^2$)	3.043 ± 0.359	3.363 ± 0.575	3.148 ± 0.233	3.244 ± 0.250	3.18 ± 0.17
TC ($\mu g/cm^2$)	14.553 ± 0.684	14.927 ± 1.015	14.995 ± 1.094	14.540 ± 0.696	15.04 ± 0.83
EC/TC	0.209 ± 0.025	0.224 ± 0.024	0.211 ± 0.017	0.224 ± 0.020	0.211 ± 0.012

132

133 **4. Conclusions**

134 This novel procedure characterizes the thermal-optical transmission instrument with a binary
135 mixture consisting of elemental carbon and sucrose. The approach incorporates a colloidal
136 suspension of carbon black that can easily be deposited onto quartz filters. As reported in Lack et

al. 2014 (*19*), there is a need for an EC surrogate for TOA, which may be fulfilled with a well-characterized carbon black suspension with properties similar to Cab-O-Jet 200. All 4 methods provided adequate results of EC, OC, EC/TC ratios, and indicated components were within the combined uncertainty of measurements and reference values. The work presented here also proves the instrument's determination of the split point can be reasonably obtained for this binary mixture of OC and EC.

A one-way analysis of variance (ANOVA) performed among the four temperature protocols (treatments) showed no difference in the protocols for either OC, EC, TC, or EC/TC at a significance level of 0.1. For example, the within-treatment mean squares for EC was larger than the between-treatment mean squares by a factor of 1.43. However, the ANOVA was based on data from only a single instrument. Other thermal-optical transmission instruments may have better measurement precision and thus lower within-treatment mean squares, which might reveal significant differences among the protocols. In addition, other formulations of the binary mixture or expanding the mixture to three or more components (e.g., EC, OC, and a metal oxide component) may result in significant differences among the protocols. Nevertheless, a water-based mixture, such as the one presented here, serves as a possible material to optimize the step temperatures and durations in TOA for correctly determining the split point, and thus to improve the quantification of BC. Additional TOA calibration mixtures with a water-soluble carbon black material should be investigated in the future.

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*Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

REFERENCES

(1) Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Karcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S. (2013) Bounding the role of black carbon in the climate system: A scientific assessment. *Journal of Geophysical Research-Atmospheres 118*, 5380-5552.

(2) Ahmed, T., Dutkiewicz, V. A., Shareef, A., Tuncel, G., Tuncel, S., and Husain, L. (2009) Measurement of black carbon (BC) by an optical method and a thermal-optical method: Intercomparison for four sites. *Atmospheric Environment 43*, 6305-6311.

(3) Hansen, A. D. A., Rosen, H., and Novakov, T. (1984) THE AETHALOMETER - AN INSTRUMENT FOR THE REAL-TIME MEASUREMENT OF OPTICAL-ABSORPTION BY AEROSOL-PARTICLES. *Science of the Total Environment 36*, 191-196.

(4) Hadley, O. L., Corrigan, C. E., and Kirchstetter, T. W. (2008) Modified Thermal-Optical Analysis Using Spectral Absorption Selectivity To Distinguish Black Carbon from Pyrolized Organic Carbon. *Environmental Science & Technology 42*, 8459-8464.

(5) Khan, B., Hays, M. D., Geron, C., and Jetter, J. (2012) Differences in the OC/EC Ratios that Characterize Ambient and Source Aerosols due to Thermal-Optical Analysis. *Aerosol Science and Technology 46*, 127-137.

(6) Conny, J. M., Norris, G. A., and Gould, T. R. (2009) Factorial-based response-surface modeling with confidence intervals for optimizing thermal-optical transmission analysis of atmospheric black carbon. *Analytica Chimica Acta 635*, 144-156.

(7) Conny, J. M., Klinedinst, D. B., Wight, S. A., and Paulsen, J. L. (2003) Optimizing thermal-optical methods for measuring atmospheric elemental (black) carbon: A response surface study. *Aerosol Science and Technology 37*, 703-723.

(8) Lappi, M. K., and Ristimaki, J. M. (2019) Comparison of filter smoke number and elemental carbon from thermal optical analysis of marine diesel engine exhaust. *Proceedings of the Institution of Mechanical Engineers Part M-Journal of Engineering for the Maritime Environment 233*, 602-609.

(9) Chen, L. W. A., Chow, J. C., Watson, J. G., Moosmuller, H., and Arnott, W. P. (2004) Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis. *Journal of Aerosol Science 35*, 765-780.

(10) Ammerlaan, B. A. J., Jedynska, A. D., Henzing, J. S., and Holzinger, R. (2015) On a possible bias in elemental carbon measurements with the Sunset thermal/optical carbon analyser caused by unstable laser signal. *Atmospheric Environment 122*, 571-576.

(11) Conny, J. M., and Slater, J. F. (2002) Black carbon and organic carbon in aerosol particles from crown fires in the Canadian boreal forest. *Journal of Geophysical Research-Atmospheres 107*.

(12) Birch, M. E., and Cary, R. A. (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology 25*, 221-241.

(13) Presser, C., Radney, J. G., Jordan, M. L., and Nazarian, A. (2019) Simultaneous transmission and absorption photometry of carbon-black absorption from drop-cast particle-laden filters. *Aerosol Science and Technology 53*, 508-525.

(14) You, R., Radney, J. G., Zachariah, M. R., and Zangmeister, C. D. (2016) Measured Wavelength-Dependent Absorption Enhancement of Internally Mixed Black Carbon with Absorbing and Nonabsorbing Materials. *Environmental Science & Technology 50*, 7982-7990.

(15) Zangmeister, C. D., Grimes, C. D., Dickerson, R. R., and Radney, J. G. Characterization and demonstration of a black carbon aerosol mimic for instrument evaluation. *Aerosol Science and Technology*, 12.

(16) Birch, M. E. (2002) Occupational monitoring of particulate diesel exhaust by NIOSH method 5040. *Applied Occupational and Environmental Hygiene 17*, 400-405.

(17) Conny, J. M. (2007) The Optimization of Thermal Optical Analysis for the Measurement of Black Carbon in Regional PM2. 5: A Chemometric Approach. *US Environmental Protection Agency, Office of Research and Development, Washington, DC, Report EPA 600*.

(18) Han, Y. M., Chen, A., Cao, J. J., Fung, K., Ho, F., Yan, B. Z., Zhan, C. L. L., Liu, S. X., Wei, C., and An, Z. S. (2013) Thermal/Optical Methods for Elemental Carbon Quantification in Soils and Urban Dusts: Equivalence of Different Analysis Protocols. *Plos One 8*, 13.

(19) Lack, D. A., Moosmuller, H., McMeeking, G. R., Chakrabarty, R. K., and Baumgardner, D. (2014) Characterizing elemental, equivalent black, and refractory black carbon aerosol particles: a review of techniques, their limitations and uncertainties. *Analytical and Bioanalytical Chemistry 406*, 99-122.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.